

ORGANIC COMPOUNDS IN GLASS MODIFICATION TECHNOLOGY (A REVIEW)

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The specifics of application of organic compounds in glass modification technology (aliphatic alcohols and ketones, organic acids and their salts, and organosilicon compounds) compared to the use of inorganic compounds are considered. It is demonstrated that treatment of the glass surface with organic compounds can improve mechanical, chemical, calorimetric, biochemical, and other properties of glasses.

Organic chemistry has long entered into all sectors of industry, including the glass production technology. The predictability and the regularity of organic reactions make it possible to predict the properties of such complicated material as glass after its modification with organic compounds.

Obviously, the use of organic compounds for modification of glass to a large extent is complicated by the fact that compounds formed by carbon and silicon have different melting and boiling points: organic compounds have lower melting and boiling points and are often easily destroyed at relatively low temperatures (even below 100°C), whereas inorganic compounds withstand high temperatures. At the same time, this difference can be made an advantage. In the context of current energy problems, the progress of biotechnology, and organization of small and medium-size production companies, one needs technologies for production of diversified glass articles with preset properties, which could be implemented at low temperatures on batch melting plants and have low energy consumption.

The present paper considers certain glass modification technologies using organic compounds, their reaction mechanisms, and the properties of the glasses obtained.

Organic compounds most frequently are used in the form of solutions, in particular, as solvents. A method for chemical interaction between the glass surface and aqueous solutions of acids and salts was pro-

posed, developed, and investigated under the guidance of I. V. Grebenschchikov and later studied in detail by N. V. Suvkovskaya with respect to making glasses with metal-oxide coatings, and by V. V. Moiseev in the context of ion exchange [1–3].

When modifying a glass surface using solid-phase spray deposition of aqueous lithium salt solutions, we observed numerous instances of glass destruction due to thermal shocks, with the deposited solution rolling off the glass surface and the deposited layer being nonuniform. To eliminate these defects, certain low-molecular (primary or secondary) one-atom saturated alcohols with the C₂–C₄ carbon chain were introduced into aqueous salt solutions. The best results were

TABLE 1

Solution composition*	Temperature, °C	Duration, min	Layer thickness, μm	Glass properties		
				central symmetric bending strength, ** MPa	light transmission, %	weight content of Li ₂ O, *** %
1 : 1 + 10% ethanol	300	120	25	85	65	1.74
	400	60	20	177	61	1.69
1 : 1 + 20% ethanol	300	120	26	97	71	2.17
	400	60	19	123	66	1.68
1 : 1 + 10% propanol-2	300	120	18	90	70	0.97
	400	60	27	119	65	1.32
1 : 1 + 20% propanol-2	300	120	17	100	63	1.13
	400	60	18	90	61	2.70

* The first two figures indicate the ratio of saturated solutions LiCl : LiNO₃ : LiSO₄ to KCl : KNO₃ : K₂SO₄, the third figure means the quantity of alcohol added up to 100%.

** The central symmetric bending strength of non-treated vertical-drawing glass 2 mm thick was 82 MPa.

*** The removed layer thickness was approximately 100 μm.

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obtained in adding ethanol and propanol-2 to aqueous solutions (Table 1).

The use of aqueous-alcohol solutions leads to the formation of a sufficiently thick salt layer on the glass surface, which facilitates the incorporation of lithium ions into the glass and increases the glass strength. Furthermore, as was earlier demonstrated (U.S. Patent No. 4133665) and later confirmed by our studies, aqueous-alcohol solutions themselves can improve the properties of glass both in hydration and due to leaching of its surface (Table 2). It is established that the weight of glass samples significantly decreases, whereas their central symmetric bending strength and impact strength increases (Table 2). However, the duration of such treatment is 10–12 h.

Salts of inorganic acids were once commonly used at the early stages of the development of technology for glass strengthening by ion exchange and deposition of metal-oxide coatings. However, such glasses had several drawbacks, since they did not have satisfactory optical properties. In the course of such treatment, along with cation exchange, for instance, when chlorides are used, anion exchange takes place as well with incorporation of the inorganic acid anion into the glass structure, which impairs its properties. This is true of the processes of glass surface modification using the ion exchange method (both high- and low-temperature) in salt melts and also in solid-phase spraying of aqueous solutions. It is established that the use of metal salts of organic acids eliminates some of these drawbacks. To modify glass surface, metal acetates and other derivatives of metal and carbon acids are applied.

We have studied the effect of organic and inorganic lithium salt additives (acetate and chloride) added to aqueous-alcohol solutions used to treat the surface of a silicate glass (Table 3). It can be seen that in both cases the mechanical properties of glass improve. However, the light transmission in the visible range in samples treated with lithium acetate is 87–89%, and in samples treated with chloride, it is only 82–84%. The light transmission of the initial glass is 89%.

An organic component has especially numerous manifestations in synthesis of oxide-metallic coatings, making it possible to obtain finely dispersed solutions. An increase in solution dispersion, on the one hand, increases the number of drops and their concentration per volume unit, which expands

TABLE 2

Solu-tion	Alcohol	Alcohol : water ratio	Tempe- rature, °C	Duration, h	Weight loss in anne- aling, %	Strength at	
						central symmetric bending, MPa*	falling from height, cm**
1	Ethanol	0 : 1	200	10	15.0	90	80
2		1 : 1	195	10	14.7	130	120
3		1.5 : 1	205	10	13.0	160	160
4		2 : 1	203	10	12.7	150	140
5	Propanol-1	0 : 1	180	12	13.0	120	150
6		1 : 1	190	12	10.5	100	140
7		1.5 : 1	200	12	11.0	80	110
8		2 : 1	200	12	12.1	140	120
9	Propanol-2	0 : 1	210	10	12.0	120	100
10		1 : 1	195	10	11.9	130	80
11		1.5 : 1	200	10	11.8	120	130
12		2 : 1	205	10	10.5	140	140
13	Butanol-1	0 : 1	180	12	10.0	90	100
14		1 : 1	200	12	9.7	100	160
15		1.5 : 1	170	12	9.5	90	130
16		2 : 1	204	12	9.1	80	90

* Average central symmetric bending strength of non-treated samples was 70 MPa.

** The non-treated sample fractured when the sphere fell from height 65 cm.

the reaction zone by means of increasing the total surface area of a solution, and on the other hand, a smaller size of drops allows for their more uniform and dense distribution over the treated surface [4]. As a consequence of the reaction

TABLE 3

Solu-tion*	Lithium salt content, g per 100 g of solution		Treatment conditions		Heat resistance, °C**	Glass strength		
	acetate	chloride	tempera- ture, °C	duration, h		micro- hardness, MPa***	central symmetric bending, MPa	falling from height, cm****
2	2.0	–	200	20	–	–	164	130
4	2.0	–	200	20	120	5200	157	140
6	1.5	–	205	10	–	–	140	150
8	1.5	–	205	10	–	–	201	160
10	1.0	–	190	12	–	–	124	120
12	1.0	–	190	12	–	–	140	140
14	2.0	–	200	12	110	4900	120	170
16	2.0	–	200	12	115	5100	132	140
2	–	1.5	180	12	–	–	137	130
4	–	1.5	180	12	110	5150	120	120
6	–	2.0	200	10	100	5080	140	150
8	–	2.0	200	10	115	4950	152	160
10	–	1.0	190	12	–	–	110	140
12	–	1.0	200	12	–	–	150	110
14	–	2.0	200	14	–	–	100	120
16	–	2.0	200	14	95	4850	90	140

* Solution composition is indicated in Table 2.

** Heat resistance of initial glass 90°C.

*** Data for non-treated glass are indicated in Table 2.

**** Microhardness of initial glass 4800 MPa.

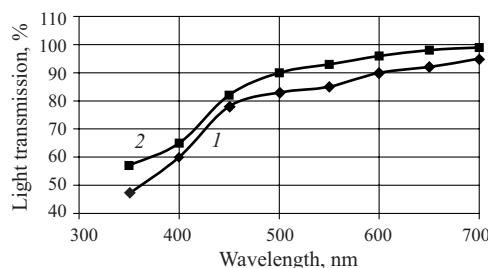


Fig. 1. Optical characteristics of glasses with iron-bearing coatings: 1) aqueous solution; 2) aqueous-acetone solution.

between the film-forming salt and the aqueous-alcohol or aqueous-acetone mixture, an metal-oxide coating is synthesized on the glass surface. The solid metal oxide at the moment of its formation is adsorbed on the glass surface and reacts with this surface being distributed in the form of a thin transparent film. The mechanism of formation of metal oxide coating on glass surface is discussed in detail in [5].

Figure 1 gives the optical characteristics of glasses with iron-bearing coatings obtained on the basis of 15% aqueous and aqueous-acetone solutions of iron chloride. The coatings were synthesized at 600°C for 4 sec.

Under equal conditions, aqueous-acetone solutions yield coatings with higher light transmission, since they are denser and more transparent. These coatings have better mechanical properties: the microhardness of glass 1 is 4300 MPa, and that of glass 2 is 4490 MPa (the microhardness of the initial glass is 4250 MPa); the abrasion resistance of glass 1 is 18.0 mg/cm², and that of glass 2 is 16.9 mg/cm² (that of initial glass is 18.8 mg/cm²).

The water resistance of such coatings determined as the amount of Na₂O released into water is shown in Fig. 2. Compared to aqueous solutions, the water resistance of iron-bearing film coatings based on aqueous-acetone solutions is higher for any concentration.

TABLE 4

Acid	Solution concentration, M	pH	Temperature, °C	Duration, min	Bending strength of sample, MPa*	Microhardness under load 50 nm, MPa**
Aminoethanoic (glycine)	0.75	7.0	90	60	120	5750
	0.75	7.0	90	120	131	5090
	0.75	7.0	90	180	125	4230
	0.75	7.0	90	240	140	4250
	0.75	7.0	90	300	130	4200
2-aminopropanoic (alanine)	0.50	7.5	80	60	150	4900
2-amino-3-hydroxybutanoic (threonine)	0.50	7.4	80	60	150	5800
2-oxypropanoic (lactic)	0.50	7.5	80	60	100	4100
2,3-dihydroxybutanoic (tartaric)	0.50	7.5	80	60	120	4050

* Strength of initial glass 70 MPa.

** Microhardness of initial glass 3640 MPa.

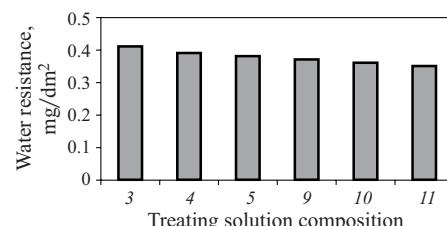
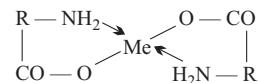


Fig. 2. Water resistance variation chart for iron-bearing film coatings: 3, 4, 5) 15, 25, 35% aqueous solutions; 9, 10, 11) respective aqueous-acetone solutions.

Even more interesting results were obtained using bi- and polyfunctional organic compounds. Such compounds, as a rule, contain several active functional groups (NO₂, OH, COOH, etc.) or easily transformable groups (OR), which are capable of forming chelate chemical complexes with metal cations on glass:



The results of the study of treating phosphate glass with amino- and oxycarbon acids are discussed in [6]. The obtained results are corroborated by the data supplied by other researchers (Gr. Britain Patent No. 1515311, U.S. Patent No. 3718488). U.S. Patent No. 3718488 describes using chelate palladium compounds to produce a metal oxide coating in decomposition. The mechanism of the process, in which oxy- and aminocarbon acids are used, is not yet quite clear. Most probably, the formation of such compounds on glass surface keeps cracks from further propagation. The properties of glasses with the specified coatings are virtually not yet studied.

This method is valuable, as it allows for improvement of mechanical properties of phosphate glasses, since the standard methods here are not suitable. However, in our opinion, this method can be regarded as a method for surface protection rather than one of glass strengthening. Silicate glasses normally do not enter into such reactions. However, in the case of a special preparation, their mechanical properties can be improved (Table 4). It can be seen that the bending strength and microhardness of glass increase. The disadvantage of this method is its long treatment duration, and its advantage consists in its low treatment temperature.

The use of organosilicon compounds for improving the service properties of glass has become known relatively recently, but the interest of researchers in this subject constantly grows, since it has become possible

on the basis of these compounds to develop materials that have no natural analogs [2, 7, 8].

We investigated the synthesis of 3-aminopropyl triethoxysilane on glass surface with subsequent tinting of glass using organic acid pigments, which cannot tint the glass directly. It is believed that such reaction is an electrophilic substitution reaction [9] and proceeds in three stages.

The obtained coatings not only tint the glass but also improve its service properties [5].

Such studies currently attract special interest in the context of the development of new biotechnologies, in which inorganic carriers are used to immobilize enzymes, bacterial cells, etc., as well as of sol-gel technologies [10, 11].

Thus, using organic compounds to modify the surface of silicate glasses has a positive effect on the treatment processes by decreasing the temperature of treatment. At the same time, the mechanical, chemical, optical, colorimetric, biochemical, and other properties of the glass improve.

The regularities of reactions of organic compounds and the results obtained by numerous researchers indicate that the use of organic compounds is one of the most promising lines in glass modification technology.

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